

Cu₂O shape transition during Cu-Au oxidation

Scientific Achievement

Using *in situ* dynamic transmission electron microscopy, we demonstrate that the Cu₂O islands that form during exposure of (001) Cu-Au alloys to oxygen at high temperatures undergo a remarkable transformation from an initially compact morphology to a dendritic structure as growth proceeds. Correspondingly, the surface composition becomes non-uniform and the fractal dimension associated with the oxide islands evolves from 2.0 to a stable value of 1.87, indicating a transition in the rate-limiting mechanism of oxidation from oxygen surface diffusion to diffusion of copper through the increasingly gold-rich regions adjacent to the islands. Our theoretical analysis based on Fick's diffusion equations indicates that the non-uniform partition of Au atoms is an intrinsic behavior for the compact growth of the oxide island, and high Au accumulation occurs in the regions adjacent to the island edges, and low Au accumulation adjacent to the island corners.

Significance

The insight obtained from this work has positive impact on the development of strategies for growing protective oxides. The formation of a protective oxide layer on a metal surface requires the rapid formation of a continuous film that impedes further oxidation by requiring bulk diffusion through the oxide. A general strategy for the protection of underlying metals is alloying, which leads to the formation of a protective oxide layer over the alloy surface due to the preferential oxidation of one component of the alloy. In order to achieve protective behavior, the oxide layer must be continuous, since the existence of discontinuities in the oxide layer leads to rapid diffusion paths. However, it is still not generally understood which alloying elements improve the likelihood of forming a protective oxide and which degrade behavior due to complicating thermodynamic and kinetic factors. The dendritic transition causes a discontinuous morphology of the oxide, which is not desirable in many technological applications. In order to grow continuous, protective oxide films, it is necessary to nucleate a large number density of oxide islands, which will lead to full coalescence of the oxide islands prior to their dendritic transition. Therefore, this dendritic transition imposes a limitation on the oxidation conditions (*i.e.*, high pO₂) to grow a continuous and protective oxide film. On the other hand, creation of complex patterns on surfaces is a fascinating area of interest in many fields. Our results suggest a new approach to growing dendritic oxide patterns on metal surfaces.

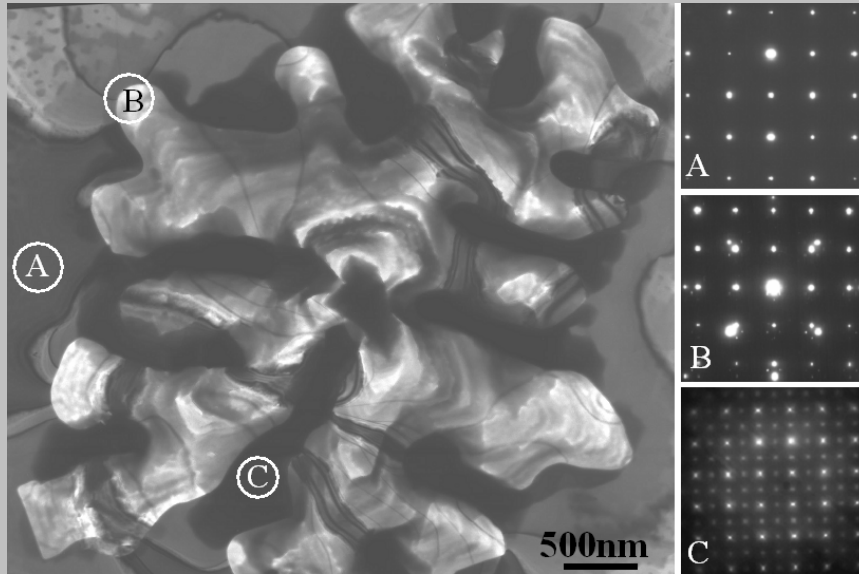
Performers

G.-W. Zhou, J.A. Eastman, R.C. Birtcher, P.M. Baldo, J. Pearson (ANL-MSD)

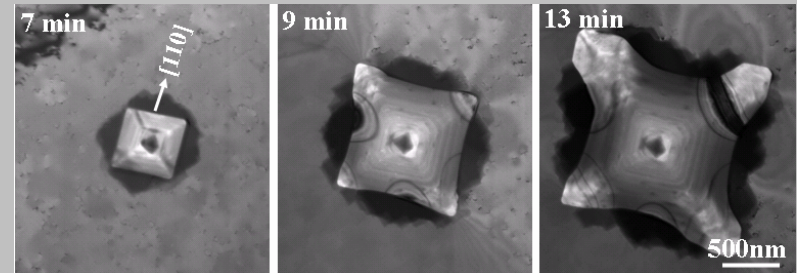
J.C. Yang, L. Wang, (U of Pittsburgh)

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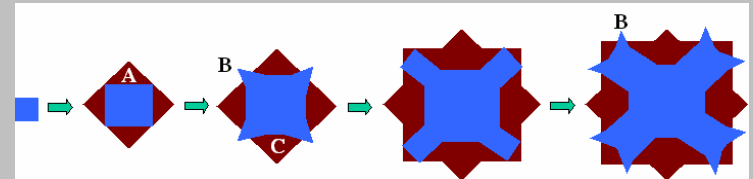
Effect of oxide island morphology on the formation of protective oxides on metal alloys



Typical morphology of dendritic oxide islands obtained during oxidation of (001)Cu-15at.%Au films at 600°C in pO₂=5×10⁻⁴ Torr. The diffraction patterns indicate Cu-Au solubility (A), epitaxial Cu₂O islands on Cu-Au alloy (B); CuAu₃ ordered phase (C)



In-situ TEM observation of dendritic transition during (001)Cu-5%Au oxidation at 600°C



Dendritic oxide growth in the oxidation of Cu-Au alloys, A: Au-rich zone, B: growth limited by oxygen surface diffusion, C: growth limited by Cu diffusion through a Au-rich zone.

- Cu₂O islands undergo a dendritic transition from initially compact shape as growth proceeds during Cu-Au oxidation
- Dendritic morphology of oxide islands prevents formation of continuous, protective oxide overlayer on metal alloys